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(54) Title: BLEACH CATALYST COMPOSITION			
(57) Abstract			
<p>There is provided a bleach catalyst composition in the form of non friable composite granules, whereby each granule is substantially free from easily oxidisable organic materials and comprises a carrier material, a binding agent, and a bleach catalyst including a source of Mn and a ligand, said ligand being a macrocyclic organic compound of the formula (I): $[NR^2-(CR^1(R^3))_q]_t$, wherein t is an integer from 2 to 3; s is an integer from 3 to 4; q is zero or one; R¹ and R² are each independently selected from H, alkyl, aryl, both optionally substituted; and R³ is independently selected from hydrogen, alkyl, aryl, both optionally substituted. These bleach granules have been found to give improved bleaching performance on specific stain-types, particularly on cocoa stains.</p>			

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BLEACH CATALYST COMPOSITION

Field of the invention

This invention relates to bleach catalyst compositions. In particular, it relates to bleach catalyst compositions comprising a manganese complex as the active bleach catalyst in a form which is suitable for use in or with a detergent and/or bleach composition. The invention also relates to a process for manufacturing bleach catalyst compositions.

Background of the invention

A variety of manganese complexes have been proposed as catalysts for enhancing the activity of peroxygen bleaches such as hydrogen peroxide, hydrogen peroxide liberating or generating compounds and inorganic and organic peroxyacids. They include manganese-gluconate complexes as described in EP-A-237 111 and manganese polyol complexes as described in EP-A-443 651.

The effective amount of such manganese complexes needed in detergent and/or bleach compositions is of the order of hundredths of a percent. The problems associated with using small quantities of materials include the difficulty of accurately dosing the material and achieving a homogeneous distribution thereof in the compositions. In order to ensure the performance of, for example, a detergent composition is consistent, it is essential that individual components of the compositions are homogeneous distributed throughout the composition.

Whilst spraying a solution of the manganese complex, hereinafter referred to as the "bleach catalyst" onto the base detergent formulation may result in a very good distribution it may also involve direct contact between the bleach catalyst and the other ingredients included in the base formulation, for example nonionic detergent active and

peroxygen bleaching agent. This may result in a reduction in the levels of active ingredient as a result of redox reactions.

- 5 Another option would be to mix pure crystals of the catalyst with a particulate detergent composition. However, this may also result in interactions between individual components with consequential loss in levels of active components.

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Previously, in order to overcome similar problems, it has been proposed to form heavy metal complexes into agglomerates prior to addition to a detergent base formulation. For example US patent 4 626 373 teaches

- 15 manganese complexes comprising Mn(II) and a ligand such as ethylenediamine tetraacetic acid or diethylene triamine pentaacetic acid may be protected by encapsulating them in a matrix of a water-soluble or water-dispersible material. The encapsulates can then be added to a base detergent
20 formulation.

Our copending European Patent Application 92310504.3 teaches granules comprising specific di- or mononuclear manganese complexes or precursors, a binding agent selected
25 from polymers, silicates and fatty acid soap mixtures and, preferably an inert chloride or carbonate salt.

We have now found that granules comprising the di- and mono nuclear manganese complexes described in the aforementioned
30 reference together with a specific selection of carrier materials when incorporated into detergent and/or bleaching compositions give improved bleaching performance on specific stain types and, in particular, on cocoa stains.

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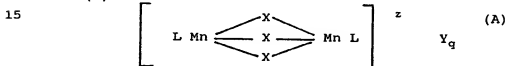
We have also found that composite granules comprising a

- mixture of fatty acids or salts thereof, a manganese complex catalyst as herein defined and a dispersing agent when prepared according to the method of the invention, show also good bleach activity, particularly on cocoa stains and good storage stability.

Definition of the invention

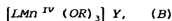
- Accordingly the invention provides a bleach catalyst composition in the form of non-friable composite granules characterised in that each granule is substantially free from easily oxidisable organic materials and comprises:

- i) a manganese complex catalyst selected from



- wherein Mn is manganese which can independently be in the III or IV oxidation state;
 X is independently a coordinating or bridging species selected from the group consisting of H_2O , O^{2-} , O_2^{2-} , $-\text{OH}$, HO_2^- , SH^- , S^{2-} , $>\text{SO}$, Cl^- , SCN^- , N_3^- , RSO_3^- , RCOO^- , NH_2^- and NR_3 , with R being H, alkyl, aryl, both optionally substituted, and R^1COO , where R^1 is an alkyl, or aryl radical, both optionally substituted;
 L is a ligand which is an organic molecule containing a number of nitrogen which coordinates via all or some of its nitrogen atoms to the manganese centres;
 Z denotes the charge of the complex and is an integer which can be positive or negative;
 Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and
 $q = z / [\text{charge Y}]$;

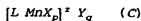
(b)



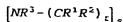
wherein Mn is manganese in the +4 oxidation state;
 5 R is a C₁-C₂₀ radical selected from the group alkyl, cycloalkyl, aryl, benzyl and radical combinations thereof;

at least two R radicals may also be connected to one another so as to form a bridging unit between two
 10 oxygens that coordinate with the manganese; .
 L is a ligand selected from a C₃-C₆₀ radical having at least 3 nitrogen atoms coordinating with the manganese; and
 Y is an oxidatively-stable counterion dependent; and

(c)



wherein Mn can be either in the II, III or IV
 20 oxidation state; each X independently represents a coordinating species selected from Cl⁻, Br⁻, I⁻, F⁻, NCS⁻, N₃⁻, I₃⁻, NH₃, RCOO⁻, RSO₃⁻, RSO₄⁻ in which R is alkyl or aryl, both optionally substituted, OH⁻, O₂²⁻, HOO⁻, H₂O, SH, CN⁻, OCN⁻, S₄²⁻ or mixtures thereof; p
 25 is an integer from 1-3; z denotes the charge of the complex and is an integer which can be positive, zero or negative; Y is a counter-ion the type of which is dependent upon the charge z of the complex; q = z/[charge Y]; and L is a ligand being a macrocyclic
 30 organic molecule of the following formula:



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wherein t is 2; s is 3 and R¹, R² and R³ can each independently be H, C₁-C₆ alkyl, or aryl, both optionally substituted;

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ii) a carrier material selected from zeolite, alkali metal sulphate, citric acid, succinic acid and starch; and

10

iii) a binding agent selected from water-soluble non-oxidisable polymers, alkalimetal silicates, saturated fatty acids, fatty acid soaps and mixtures thereof.

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The invention also provides a method for preparing a bleach catalyst composition in the form of non-friable granules, said composition comprising at least two fatty acids or salts thereof, a manganese complex catalyst as herein defined and a dispersing agent, and said method comprising the steps of

20

- (i) forming a melt of the fatty acids or salts thereof;
- (ii) adding the manganese complex catalyst and dispersing agent to said melt; and
- (iii) spray-cooling the resulting mixture.

25

The invention further provides a detergent composition comprising non-friable composite granules comprising a manganese complex catalyst as hereinbefore defined, a carrier material and a binding agent.

Detailed description of the invention

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As explained above, the granules of the present invention, when incorporated into detergent compositions, show improved bleaching performance on cocoa stains. Without being bound by theory, this is believed to be due to the fact that the bleach catalyst in the granules according to

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the invention is released at a slower rate, ie bleaching does not occur immediately when the detergent composition is contacted with water and therefore the other components

in the detergent composition such as the surface active materials have time to start to perform their function before bleaching occurs.

- 5 A further advantage of the granules according to the invention is that storage stability, particularly in detergent compositions containing high levels of nonionic detergent active material such as 15 to 25% by weight is improved.

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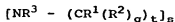
The granule according to the invention is substantially free from easily oxidisable organic material, especially primary and secondary alcohols: these easily oxidisable materials are present at levels of less than 1% by weight of the granule. The granule preferably comprises 0.5 to 20%, most preferably from 1 to 15% by weight of a manganese complex catalyst, from 5 to 90% by weight of a carrier material and from 5 to 91% by weight of the binding agent.

20

When the manganese complex is a complex of formula (A), preferred complexes are those in which X is either CH_3COO^- or O^{2-} or mixtures thereof, most preferably wherein the manganese is in the IV oxidation state and X is O^{2-} .

- 25 Preferred ligands are those which contain at least three nitrogen atom and which coordinate via three nitrogen atoms to one of the manganese centres, and are of a macrocyclic nature. Particularly preferred ligands are those of formula:

30



wherein t is an integer from 2 to 3; s is an integer from 3 to 4; q is zero or one; R^1 and R^2 are each independently selected from H, alkyl, aryl, both optionally substituted; and R^3 is independently selected from hydrogen, alkyl, aryl, both optionally substituted and, in particular,

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- (1) 1,4,7-trimethyl-1,4,7-triazacyclononane, (Me₃-TACN),
and
- (2) 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, (Me₄-TACN).

5

The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and can be selected from, for example, chloride; sulphate; nitrate; methylsulphate; surfactant-anions, such as the long-chain
10 alkylsulphates, alkylsulphonates, alkylbenzenesulphonates, tosylate; trifluormethylsulphonate; perchlorate (ClO₄⁻), BPh₄⁻ and PF₆⁻, though some counter-ions are more preferred than others for reasons of product property and safety.

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Consequently the preferred dinuclear manganese complexes usable in the granules of the present invention are:

- (I) [(Me₃-TACN) Mn^{IV}(μ-O)₃Mn^{IV}(Me₃-TACN)]²⁺(PF₆⁻)₂
- 20 (II) [(Me₄-TACN) Mn^{IV}(μ-O)₃Mn^{IV}(Me₄-TACN)]²⁺(PF₆⁻)₂
- (III) [(Me₃-TACN) Mn^{III}(μ-O)(μ-OAc)₂Mn^{III}(Me₃-TACN)]²⁺(PF₆⁻)₂
- (IV) [(Me₄-TACN) Mn^{III}(μ-O)(μ-OAc)₂Mn^{III}(Me₄-TACN)]²⁺(PF₆⁻)₂

which are hereinafter also abbreviated as:

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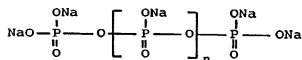
- (I) [Mn^{IV}₂(μ-O)₃(Me₃-TACN)₂](PF₆)₂
- (II) [Mn^{IV}₂(μ-O)₃(Me₄-TACN)₂](PF₆)₂
- (III) [Mn^{III}₂(μ-O)(μ-OAc)₂(Me₃-TACN)₂](PF₆)₂
- (IV) [Mn^{III}₂(μ-O)(μ-OAc)₂(Me₄-TACN)₂](PF₆)₂

30

When the manganese complex is a mononuclear complex of formula (B), preferred complexes are those in which L is selected from 1,4,7-trimethyl-1,4,7-triazacyclononane and 2-methyl-1,4,7-trimethyl-1,4,7-triazacyclononane and R is a
35 C₁ alkyl. Such mononuclear complexes are further described in Applicants copending US Patent Application No 07/798 396.

Mononuclear complexes of formula (C) are further described in Applicants copending European Patent Application No. 93211580.2

- 5 Preferably the granules are coated with non-oxidisable water-soluble material. Suitable materials include organic homopolymers or heteropolymers, organic nonionic compounds, long-chain C_{10} - C_{22} fatty acids and fatty acids soaps and the so-called glassy sodium phosphates of the following
- 10 molecular structure.



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wherein the average value of n is from about 10 to 30. Examples of suitable organic homo- or heteropolymers are modified starch, polyvinylpyrrolidone, polyvinylalcohol, and sodium carboxymethylcellulose.

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- Suitable nonionic compounds are for example polyethylene glycols having a molecular weight of from 1000 to 5000; C_{15} - C_{24} fatty alcohols or C_8 - C_{12} alkyl-phenols having from about 10 to 60 ethylene oxide units; and the long-chain
- 25 fatty acid alkylolamides, such as coconut fatty acid monoethanolamide.

- Preferably, the granules according to the invention will also comprise a pigment. Titanium dioxide is particularly
- 30 preferred.

- Preferably the bleach catalyst within the granules is of an average particle size as small as possible preferably below 200 μm for proper distribution and to ensure fast delivery
- 35 of the catalyst to the wash, though too small particles may cause handling problems during the granulation process. A preferred and optimum bleach catalyst particle size is

within a range of between about 50 and about 150 μ m.

- Bleach catalyst particles larger than 150 μ m may give distribution problems and are more difficult to granulate, whereas particles smaller than 50 μ m may cause handling problems and excessive granule colouration.

- Granule growth control is necessary to try to ensure the composite granules are of the same approximate size and bulk density as the main detergent or cleaning powder into which they are incorporated so as to avoid segregation by percolation or segregation by floating.

- Percolation, bringing the bleach catalyst composite granules to the bottom of a detergent powder batch, pack etc., may occur during and after mixing by vibration, handling and aeration, and will specifically happen with too small and too dense granules.
- Floating will happen specifically with granules which are too large and too light. Both phenomena should be avoided, because they introduce errors in amounts dosed to a washing machine.
- The bulk density and size of the composite granules can be controlled via the composition, the process conditions or both.

- The composite granules of the invention can be prepared by any of the conventional and known granulation techniques, such as using a pan-granulator, fluidised bed, Schugi mixer, Lödige ploughshare mixer, rotating drum and other low energy mixers; by compaction, including extrusion and tableting optionally followed by pulverising and grinding; and by a high shear-energy process using a high-speed mixer/granulator equipment having both a stirring action of high energy and a cutting action. Examples of such high-

speed mixer/granulator equipment are the Fukae (Trade Mark) FS-G mixer manufactured by Fukae Powtech Kogyo Co. Japan. Other mixers usable in the process of the invention include the Diosna (Trade Mark) V series ex. Dierks & Söhne, Germany; the Pharma matrix (Trade Mark) ex T K Fielder Ltd England; the Fuji (Trade Mark) VG-C Series ex Fuji Sangyo Co. Japan; and the Roto (Trade Mark) ex Zanchette & Co. S.r.l. Italy. Beside batch equipment, it is also possible to use a high speed mixer/granulator such as the Lodige Recycler.

Fatty acids suitable for use in the granules prepared according to the method of the invention are C₁₀-C₁₈ fatty acids and salts thereof. It is particularly preferred to use a mixture of lauric and stearic acid. The fatty acid mixture is preferably present at a level of 45 to 75% by weight of the composite granule. Particularly preferred dispersing aids for use in these granules are aluminosilicates such as zeolites present at a level of from 25 to 55% by weight. The manganese complex catalyst is preferably present at a level of from 0 to 20%, most preferably 1 to 15% by weight.

The detergent composition according to the invention may further contain ingredients commonly present in such compositions. They include surface active materials including soaps, synthetic anionic, nonionic, cationic and zwitterionic detergent surfactants preferably present in an amount from 0.5 to 50% by weight.

If the composition contains both anionic and nonionic surfactant, it is preferred that the nonionic surfactant is present in excess amount. Other ingredients include detergency builders such as aluminosilicates in particular zeolites, e.g. zeolite A, B, C, X and Y types as well as zeolite MAP as described in EP 384 070; and precipitating builders such as sodium orthophosphate and sodium

carbonate. Such builders are preferably present in an amount from 5 to 80% by weight. Other typical ingredients include enzymes, fluorescent agents, multifunctional polymers, stabilising agents such as ethylene diamine tetraacetate (EDTA) and the polyphosphonic acid derivatives (e.g. Dequest®).

Such detergent compositions can be used to bleach stained substrates by contacting the substrate in aqueous medium with the detergent composition.

The invention will now be further illustrated by the following non-limiting examples.

15 EXAMPLES

Preparation of manganese complex compound (I)

Step I: SYNTHESIS OF

20 $[\text{Mn}^{\text{III}}_2(\mu\text{-O})_1(\mu\text{-OAc})_2(\text{Me}_3\text{-TACN})_2] (\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})$

All solvents were degassed (first a vacuum was applied over the solvent for 5 minutes and subsequently argon gas was introduced; this procedure was repeated three times) prior to use (to exclude all oxygen, which oxidizes Mn^{II} to Mn^{IV} and causes the formation of $\text{Mn}^{\text{IV}}\text{O}_2$). The reaction was carried out at room temperature, under argon atmosphere, unless otherwise stated.

30 In a 25 ml round-bottomed flask, equipped with a magnetic stirrer, 500 mg (2.91 mmol) 1,4,7-trimethyl-1,4,7-triazacyclononane was dissolved in 15 ml ethanol/water (85/15). This gave a clear, colourless solution (pH >11). Then 0.45 g (1.80 mmol) $\text{Mn}^{\text{III}}\text{OAc}_3 \cdot 2\text{aq}$ was added and a cloudy, dark brown solution obtained. After the addition of 1.00 g (7.29 mmol) $\text{NaOAc} \cdot 3\text{aq}$, the pH fell to 8. About 15 drops of 70% HClO_4 solution were added to adjust the pH

- of the reaction mixture to 5.0. After addition of 1.50 g (12.24 mmol) NaClO_4 , the colour of the reaction mixture changed from brown to red within about 30 minutes. Then the reaction mixture was allowed to stand for one week at room temperature and the product precipitated in the form of red crystals. The resulting precipitate was filtered over a glass filter, washed with ethanol/water (85/15) and dried in a dessicator over KOH.

10 Step 2: SYNTHESIS OF $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{-TACN})_2](\text{PF}_6)_2\text{H}_2\text{O}$

- In a 50 ml round-bottomed flask, equipped with a magnetic stirrer, 661.4 mg of the material from step (1) (0.823 mmol crystals were pulverised, giving a purple powder) was dissolved in 40 ml of an ethanol/water mixture (1/1). After a five-minute ultrasonic treatment and stirring at room temperature for 15 minutes, all powder had dissolved, giving a dark-red-coloured neutral solution. 4 ml of triethylamine was added and the reaction mixture turned to dark-brown colour (pH >11). Immediately 3.55 g (21.12 mmol) of sodium hexafluorophosphate (NaPF_6) was added. After stirring for 15 minutes at room temperature, in the presence of air, the mixture was filtered removing some manganese dioxide, and the filtrate was allowed to stand overnight. A mixture of MnO_2 and red crystals was formed. The solids were collected by filtration and washed with ethanol. The red crystals (needles) were isolated by adding a few ml of acetonitrile to the filter. The crystals easily dissolved, while MnO_2 , insoluble in acetonitrile, remained on the filter. Evaporation of the acetonitrile solution resulted in the product as red flocks. This material was the Mn catalyst used in preparing the following granules.
- 15 In the examples which follow the composition of the base detergent powder used was as follows:-

% by weight

	Linear primary alcohol sulphate	20
	(Sodium salt)	
	Nonionic ethoxylate (3 and 7EO)	20
	Zeolite MAP*	30
5	Percarbonate	25
	Carbonate	5
	Silicate	2
	TAED	3
	Minors, including enzymes + moisture	to 100%

10

* Zeolite MAP prepared by a method similar to that described in Examples 1 to 3 of EP-A-384 070.

Experimental Storage Tests

- 15 Storage experiments were carried out in open plastic cups containing a sample of 20g of detergent powder. The cartons were stored at 37°C/70RH. The storage stability was assessed visually by estimating the percentage of composite granules which had changed from white to brown in
- 20 colour. The granules were not considered to be storage stable if, from a visual assessment, it appeared that more than about 10% of the total composite granules in the powder had changed colour from white to brown. The brown coloured is considered to be characteristic of manganese
- 25 complex catalyst in the composite granules which has through redox reactions been converted into an inactive form.

Bleach tests

- 30 Bleaching was assessed in an AEG turnette washing machine in the presence of a soiled load at a washing temperature of 30°C. Detergent compositions containing of the granules according to the examples were dosed at a level of 87g per machine cycle. The amount of composite granules added to
- 35 the detergent base formulation was adjusted to ensure that 0.04% by weight of the manganese complex catalyst was present in the wash liquor.

The reflectance ($R_{460\text{nm}}$) of two types of stained test cloth was measured before and after treatment. The change in reflectance ($\Delta R_{460\text{nm}}$) gives a measure of the effectiveness of the treatment. Reflectance ($R_{460\text{nm}}$) was measured on a Zeiss Elrephometre. The ($\Delta R_{460\text{nm}}$) results presented below are an average for 7 machine cycles with 1 test cloth per cycle. The test cloths used in the experiments were a cotton cloth stained with chocolate (cloth A) and a cotton cloth stained with cocoa milk (cloth B).

10

Example 1 - Preparation of bleach catalyst granules

1a. Mn Catalyst/Succinic Acid/Fatty Acids-Soap Granules

- A fatty acids/soap mixture was made by blending 56.2 g of lauric acid, 34.2 g of stearic acid and 9.6 g of 50% caustic solution at 70°C. A granule was produced by dry mixing 29.24 g of ground succinic acid with 0.76 g Mn catalyst crystals and subsequently adding the fatty acids/soap mixture in a high shear mixer.
- 20 The pH of this granulate in aqueous solution was 3.4, mean particle diameter of 782 μm .

1b. Mn catalyst/Zeolite/Fatty Acids-Soap Granules

- The same fatty acids-soap mixture as described above was used as the binder material for 29.16 g Zeolite and 0.84 g Mn catalyst. A granule was produced by agglomeration in a high shear mixer. pH of the material was 8.4, particle size 806 μm .

30 1c. Mn catalyst/Sodium citrate/Fatty Acids Granules

- A fatty acids blend was made by mixing 70 parts of lauric acid with 30 parts of stearic acid at 70°C.
- A granulate was produced by first dry mixing 43.0 g sodium citrate with 1.0 g Mn catalyst and subsequently adding 6.0 g of said fatty acids blend under high shear conditions. The pH of the granulate in aqueous solution

was 7.0, mean particle diameter was 836 μm .

1d. Mn catalyst/Sodium Sulphate/Fatty Acids Granules

- Under high shear a granulate was produced composed of 150 g of sodium sulphate, 3.23 g of catalyst material and 14.6 g of the fatty acids blend as described in the above example. The acidity of the sample was 5.8, the average diameter was 852 μm .

10 1e Mn catalyst/Zeolite/Fatty Acids Granules

- A fatty acids/soap mixture was made by blending 56.2 g of lauric acid 34.2 g of stearic acid and 9.6 g of 50% caustic solution at 70°C in a Lodige Recycler. Thereafter, zeolite A4 and the manganese catalyst was added. The product was cooled in a fluid bed. The nominal dry composition of the granule was
- 31.7% fatty acid soap
 - 66.2% zeolite
 - 2.1% Mn-catalyst.

20

1f Mn catalyst/Zeolite/Fatty Acids Granules

- A fatty acids/soap mixture was made by blending lauric acid, stearic acid and caustic solution. Into the resulting mixture was dispersed Mn-catalyst. This mixture was then placed in a batch Fukae mixer together with zeolite MAP and granulated. A further portion of the fatty acid soap was added together with zeolite A4. The nominal composition of the granule was
- 27% fatty acid soap
 - 33.5% zeolite MAP
 - 18.5% zeolite A4
 - 1.55 Mn catalyst.

35 Example 2 - Preparation of bleach catalyst granules by spray cooling

- 2a. 35.22 kg lauric acid and 20.21 kg stearic acid were

- 5 blended and made molten at 70°C. The resulting mixture was partly saponified by adding 6.57 kg 50% sodium caustic solution and mixing it in a high speed mixer. 25.00 kg Zeolite A4, 10.00 kg titanium dioxide and 3.00 kg Mn-catalyst were added stepwise under constant high speed mixing. After total homogenization the mixture was spray cooled in a spray tower with ambient air. The mean particle size of the product was in the range 700 to 1000 microns, with less than 0.2% below 180 microns.
- 10
- 2b. 41.42 kg lauric acid and 13.89 kg stearic acid were blended and made molten at 70°C. The resulting mixture was partly saponified by adding 6.70 kg 50% sodium caustic solution and mixing it in a high speed mixer. 25.00 kg Zeolite A4, 10.00 kg titanium dioxide and 3.00 kg Mn-catalyst were added stepwise under constant high speed mixing. After total homogenization the mixture was spray cooled in a spray tower with ambient air. The mean particle size of the product was 758 microns, with less than 0.2% below 180 microns.
- 15
- 2c. 47.93 kg lauric acid and 7.13 kg stearic acid were blended and made molten at 70°C. The resulting mixture was partly saponified by adding 6.94 kg 50% sodium caustic solution and mixing it in a high speed mixer. 25.00 kg Zeolite A4, 10.00 kg titanium dioxide and 3.00 kg Mn-catalyst were added stepwise under constant high speed mixing. After total homogenization the mixture was spray cooled in a spray tower with ambient air. The mean particle size of the product was 808 microns, with less than 0.2% below 180 microns.
- 20
- 2d. 26.03 g lauric acid and 16.45 g stearic acid were
- 25
- 30
- 35

- blended and made molten at 70°C. The mixture was partly saponified by adding 4.62 g 50% sodium caustic solution and mixing it in a high speed mixer. 48.00g starch and 3.90 g Mn-catalyst were added stepwise under constant high speed mixing. After total homogenization the mixture was spray cooled in liquid nitrogen.
- 2e. 33.38 g lauric acid and 20.32 g stearic acid were blended and made molten at 70°C. The mixture was partly saponified by adding 9.40g 42.5 % potassium caustic solution and mixing it in a high speed mixer. 34.00 g Zeolite A4 and 2.90 g Mn-catalyst were added stepwise under constant high speed mixing. After total homogenization, the mixture was spray cooled in liquid nitrogen.
- 2f A fatty acid soap mixture was made by mixing 62 parts of sodium salt of lauric acid with 38 parts of the sodium salt of stearic acid at 80°C. To the thus-formed melt were added zeolite A4 and the Mn catalyst. Thereafter, the resulting mixture was spray cooled in liquid nitrogen.
- 25 Materials used:
- Lauric acid.....: Prifrac 2920, ex Unichema
 - Stearic acid.....: Pristerene 4900, ex Unichema
 - Sodium caustic.....: ex Chemproh
 - Potassium caustic : ex Chemproh
 - Zeolite A4.....: Wessalith P, ex Degussa
 - Titanium dioxide...: ex Kronos

In the following examples, granules prepared as described above in 1e, 1f and 2f were added to the base detergent formulation described above.

The results of the bleach tests are as follows:-

Granule	1e	1f	2f
		ΔR_{460}	

Test cloth

5	A	1.6	2.1	4.2
	B	14.8	14.9	16.6

The results demonstrate the clear benefit of making granules by a route which involves spray cooling.

10

The results of the storage tests were as follows:-

Visual Stability

<u>Time/days</u>	1 day	3 days	28 days
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15	<u>Granule</u>			
	1e	No	No	Yes
	1f	No	No	No
	2f	No	No	No

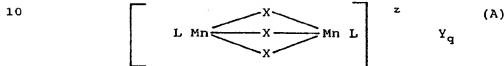
- 20 Key: - "no", when less than 10% of the bleach catalyst granules changed colour
 - "yes", when more than 10% of the bleach catalyst granules changed colour.

CLAIMS

1. Bleach catalyst composition in the form of non-friable composite granules characterised in that each granule is substantially free from easily oxidisable organic materials and comprises:

i) a manganese complex catalyst selected from

(a)



wherein Mn is manganese which can independently be in the III or IV oxidation state;

X is independently a coordinating or bridging species selected from the group consisting of H_2O , O^{2-} , O_2^{2-} , OH^- , HO_2^- , SH^- , S^{2-} , >SO , Cl^- , SCN^- , N_3^- , RSO_3^- , RCOO^- , NH_2^- and NR_3 , with R being H, alkyl, aryl, both

optionally substituted, and R^1COO , where R^1 is an alkyl, or aryl radical, both optionally substituted;

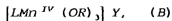
L is a ligand which is an organic molecule containing a number of nitrogen which coordinates via all or some of its nitrogen atoms to the manganese centres;

Z denotes the charge of the complex and is an integer which can be positive or negative;

Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and

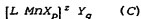
$q = z / [\text{charge Y}]$;

(b)

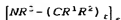


- 5 wherein Mn is manganese in the +4 oxidation state;
 R is a C₁-C₂₀ radical selected from the group alkyl,
 cycloalkyl, aryl, benzyl and radical combinations
 thereof;
 at least two R radicals may also be connected to one
 10 another so as to form a bridging unit between two
 oxygens that coordinate with the manganese;
 L is a ligand selected from a C₃-C₆₀ radical having at
 least 3 nitrogen atoms coordinating with the
 manganese; and
 15 Y is an oxidatively-stable counterion dependent;

(c)



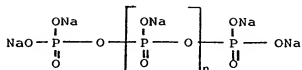
- 20 wherein Mn can be either in the II, III or IV
 oxidation state; each X independently represents a
 coordinating species selected from Cl⁻, Br⁻, I⁻, F⁻,
 NCS⁻, N₃⁻, I₃⁻, NH₃, RCOO⁻, RSO₃⁻, RSO₄⁻ in which R is
 alkyl or aryl, both optionally substituted, OH⁻, O₂²⁻,
 25 HOO⁻, H₂O, SH, CN⁻, OCN⁻, S₄²⁻ or mixtures thereof; p
 is an integer from 1-3; z denotes the charge of the
 complex and is an integer which can be positive, zero
 or negative; Y is a counter-ion the type of which is
 dependent upon the charge z of the complex; q =
 30 z/[charge Y]; and L is a ligand being a macrocyclic
 organic molecule of the following formula:



wherein t is 2; s is 3 and R¹, R² and R³ can each independently be H, C₁-C₆ alkyl, or aryl, both optionally substituted;

- 5 ii) a carrier material selected from zeolite, alkali metal sulphate, citric acid, succinic acid and starch; and
 - 10 iii) a binding agent selected from water-soluble non-oxidisable polymers, alkalimetal silicates, saturated fatty acids, fatty acid soaps and mixtures thereof.
2. Bleach catalyst composition according to claim 1, wherein the composition comprises from 1 to 15% by weight
- 15 of the manganese complex catalyst, from 5 to 90% by weight of the carrier material, and from 5 to 91% by weight of the binding agent.
3. Bleach catalyst composition according to claim 1 or 2,
- 20 wherein the manganese complex catalyst is a complex of formula (A) in which X is O²⁻ and the manganese is in the IV oxidation state.
4. Bleach catalyst composition according to claim 3,
- 25 wherein the manganese complex catalyst is selected from the group consisting of [Mn^{IV}₂(μ-O)₃(Me₃-TACN)₂](PF₆)₂, [Mn^{IV}₂(μ-O)₃(Me₄-TACN)₂](PF₆)₂, [Mn^{III}₂(μ-O)(μ-OAc)₂(Me₃-TACN)₂](PF₆)₂, [Mn^{III}₂(μ-O)(μ-OAc)₂(Me₄TACN)₂](PF₆)₂.
5. Bleach catalyst composition according to any of claims
- 30 1-4, wherein the granules are coated with non-oxidisable water-soluble material selected from organic homopolymers, organic heteropolymers, organic nonionic compounds, long-chain C₁₀-C₂₂ fatty acids and fatty acids soaps and the so-

called glassy sodium phosphates of the following molecular structure:



wherein the average value of n is from about 10 to 30.

6. Bleach catalyst composition according to any of claims 1-5, wherein the manganese complex catalyst within the granules has an average particle size in a range of between 50 and 150 μm .

7. Method of preparing a bleach catalyst composition in the form of non-friable granules, said composition comprising at least two fatty acids or salts thereof, a manganese complex catalyst as herein defined and a dispersing agent, and said method comprising the steps of
(i) forming a melt of the fatty acids or salts thereof;
(ii) adding the manganese complex catalyst and the dispersing agent to said melt; and
(iii) spray-cooling the resulting mixture.

8. Method according to claim 7, wherein a mixture of lauric acid and stearic acid are applied as the fatty acids, said mixture being present at a level of 45 to 75% by weight of the composition.

9. Method according to claim 7 or 8, wherein an aluminosilicate is applied as the dispersing agent, at a concentration of from 25 to 55% by weight of the composition.

10. Method according to any of claims 7-9, wherein the manganese complex catalyst is applied at a level of from 1 to 15% by weight of the composition.

Int: nal Application No
PCT/EP 94/00640

According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 194 416 (S.JURELL, J.KERSHER) 16 March 1993 cited in the application see column 10; claims ---	1,7
A	EP,A,0 225 663 (UNILEVER) 16 June 1987 see page 9; examples ---	1,2,5
A	EP,A,0 141 470 (UNILEVER) 15 May 1985 cited in the application see examples ---	1,2,5,7
A	US,A,4 009 113 (R.GREEN, R.JOHNSON) 22 February 1977 see examples 1,3 ---	7,8
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☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int. onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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